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<p>(54) Title of the invention Production process of ethylene wax (21) Application No. S60-078462 (22) Date of filing April 15, 1985 (72) Inventor Toshiyuki TSUTSUI 3-6, Misono 1-chome, Ohtake-shi, Hiroshima, JAPAN (72) Inventor Mamoru KIOKA 3-6, Misono 1-chome, Ohtake-shi, Hiroshima, JAPAN</p>	<p>(72) Inventor Norio KASHIWA 2-9, Murotsuki-machi 1-chome, Iwakuni-shi, Yamaguchi, JAPAN (71) Applicant Mitsui Petrochemical Industries, Ltd. 2-5, Kasumigaseki 3-chome, Chiyoda-ku, Tokyo, JAPAN (74) Agent Patent attorney Kanou YAMAGUCHI</p>
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# SPECIFICATION

## 1. Title of the invention

Production process of ethylene wax

## 5 2. Claim

(1) A process for producing ethylene wax comprising  
polymerizing ethylene or copolymerizing ethylene with an  
 $\alpha$ -olefin in the presence of a catalyst to yield a solid ethylene  
polymer having an intrinsic viscosity  $[\eta]$  of 0.4 dl/g or less,  
10 said catalyst comprising:

(A) a transition metal compound selected from Groups IVb,  
Vb and VIb of the periodic table, and

(B) aluminoxane.

## 3. Detailed description of the invention

## 15 [Field of the invention]

The present invention relates to a production process  
of ethylene wax, particularly to a production process of

ethylene wax having narrow molecular weight distribution. More particularly, the invention relates to a process for efficiently producing such ethylene wax with use of a highly active catalyst.

5 [Background of the invention]

Industrial production of low molecular weight olefin polymers such as polyethylene wax generally employs titanium catalysts. Such catalysts are highly active and provide low molecular weight polymers in high yields per unit quantity of  
10 the catalyst. However, they require high hydrogen partial pressure in the gas phase in the polymerization system, resulting in formation of by-product alkane in large quantity. Furthermore, the resultant low molecular weight polymers have wide molecular weight distribution. Particularly, low  
15 molecular weight polymers having molecular weights of 1000 or less become too sticky unless lower molecular weight fractions are removed. This makes it difficult to use them as pigment dispersants, resin processing aids, printing ink and paint additives, rubber processing aids and fiber treating agents.  
20 To overcome such problems, JP-A-S59-210905 discloses a process for producing low molecular weight polymers using a vanadium catalyst. The publication describes that the production can provide low molecular weight polymers having narrow molecular weight distribution under lower hydrogen partial pressure than

by use of a titanium catalyst. This process attains some positive results, but is still to be improved.

[Means for solving the problem and Summary of the invention]

A process for producing ethylene wax according to the present invention comprises polymerizing ethylene or copolymerizing ethylene with an  $\alpha$ -olefin in the presence of a catalyst to yield a solid ethylene polymer having an intrinsic viscosity  $[\eta]$  of 0.4 dl/g or less, the catalyst comprising:

- (A) a transition metal compound selected from Groups IVb, Vb and VIb of the periodic table, and
- (B) aluminoxane.

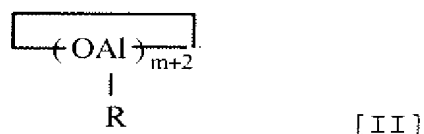
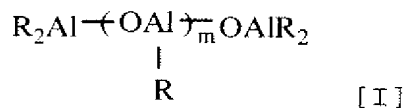
The transition metal compound (A) for the catalyst used in the invention is a compound of a transition metal selected from Groups IVb, Vb and VIb of the periodic table. Examples thereof include titanium, zirconium, hafnium, vanadium and chromium compounds. Of these transition metal compounds, titanium and zirconium compounds are preferable, and zirconium compounds are particularly preferred because of high activity. The transition metal compound preferably contains a hydrocarbon group or both a hydrocarbon group and a halogen atom. Particularly preferably, it contains at least one, especially two hydrocarbon groups and at least one, especially two halogen atoms. Exemplary hydrocarbon groups include alkyl groups such as methyl, ethyl, n-propyl, isopropyl, n-butyl,

sec-butyl, tert-butyl, isobutyl and neopentyl; alkenyl groups such as isopropenyl and 1-butenyl; cycloalkadienyl groups such as cyclopentadienyl and methylcyclopentadienyl; and aralkyl groups such as benzyl and neophyl. Of the above hydrocarbon groups, the cycloalkadienyl groups are preferable, and the cyclopentadienyl group is particularly preferred. The halogen atoms include fluorine, chlorine, bromine and iodine. Specific examples of the transition metal compounds include titanium compounds such as

- 10 bis(cyclopentadienyl)dimethyltitanium,  
bis(cyclopentadienyl)diethyltitanium,  
bis(cyclopentadienyl)diisopropyltitanium,  
bis(cyclopentadienyl)methyltitanium monochloride,  
bis(cyclopentadienyl)ethyltitanium monochloride,
- 15 bis(cyclopentadienyl)isopropyltitanium monochloride,  
bis(cyclopentadienyl)methyltitanium monobromide,  
bis(cyclopentadienyl)methyltitanium monoiodide,  
bis(cyclopentadienyl)titanium difluoride,  
bis(cyclopentadienyl)titanium dichloride,
- 20 bis(cyclopentadienyl)titanium dibromide and  
bis(cyclopentadienyl)titanium diiodide; zirconium compounds such as bis(cyclopentadienyl)dimethylzirconium,  
bis(cyclopentadienyl)diethylzirconium,  
bis(methylcyclopentadienyl)diisopropylzirconium,

bis(cyclopentadienyl)methylzirconium monochloride,  
 bis(cyclopentadienyl)ethylzirconium monochloride,  
 bis(cyclopentadienyl)methylzirconium monobromide,  
 bis(cyclopentadienyl)methylzirconium monoiodide,  
 5 bis(cyclopentadienyl)zirconium difluoride,  
 bis(cyclopentadienyl)zirconium dichloride,  
 bis(cyclopentadienyl)zirconium dibromide,  
 bis(cyclopentadienyl)zirconium monochloride monohydride and  
 bis(cyclopentadienyl)zirconium diiodide; hafnium compounds  
 10 such as bis(cyclopentadienyl)dimethylhafnium,  
 bis(cyclopentadienyl)methylhafnium monochloride and  
 bis(cyclopentadienyl)hafnium dichloride; and vanadium  
 compounds such as bis(cyclopentadienyl)vanadium dichloride  
 and bis(cyclopentadienyl)vanadium monochloride.

15 The aluminoxane (B) for the catalyst used in the  
 invention may be exemplified with organoaluminum compounds  
 represented by the formula [I] or [II]:



20 wherein R is a hydrocarbon group and m is an integer of 2 or  
 greater. In the aluminoxane, the hydrocarbon group R is methyl,  
 ethyl, propyl or butyl group, preferably methyl or ethyl group,

and particularly preferably methyl group. Also, the integer m is 2 or greater, preferably 5 or greater, and particularly preferably from 10 to 100. For example, the aluminoxane may be prepared by the following processes.

5           (1) Trialkylaluminum is added to a hydrocarbon medium suspension of a compound containing absorbed water or a salt containing water of crystallization (such as copper sulfate hydrate or aluminum sulfate hydrate), to carry out reaction.

          (2) Water is allowed to act directly on trialkylaluminum  
10   in such a medium as benzene, toluene, ethyl ether or tetrahydrofuran.

Of the processes, the process (1) is preferable. The aluminoxane may contain small amounts of other components, such as organometallic components.

15           In the process of the present invention, ethylene or a mixture of ethylene and other  $\alpha$ -olefin is fed to the polymerization system. The  $\alpha$ -olefins other than ethylene include those of 3 to 20 carbon atoms, such as propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene,  
20   1-dodecene, 1-tetradecene, 1-hexadecene, 1-octadecene and 1-eicosene. These  $\alpha$ -olefins may be used in combination of two or more kinds. The olefin polymerization material(s) in the polymerization system will generally contain ethylene in an amount of 60 to 100 mol%, preferably 70 to 100 mol%, and the

$\alpha$ -olefin(s) in an amount of 0 to 40 mol%, preferably 0 to 30 mol%.

In the process of the invention, polymerization is performed in a hydrocarbon medium. Examples of the hydrocarbon medium include aliphatic hydrocarbons such as butane, isobutane, pentane, hexane, octane, decane, dodecane, hexadecane and octadecane; alicyclic hydrocarbons such as cyclopentane, methylcyclopentane, cyclohexane and cyclooctane; aromatic hydrocarbons such as benzene, toluene and xylene; and petroleum fractions such as gasoline, kerosine and gas oil. The polymerization material olefin may be used as the hydrocarbon medium. Of the above hydrocarbon media, the aromatic hydrocarbons are preferred.

In carrying out liquid phase polymerization according to the process of the present invention, the transition metal compound is used in an amount in terms of the transition metal atom of  $10^{-8}$  to  $10^{-2}$  g, and preferably  $10^{-7}$  to  $10^{-3}$  g per liter of the polymerization system. The aluminoxane is used in an amount in terms of aluminum atom of  $10^{-4}$  to  $10^{-1}$  g, and preferably  $10^{-3}$  to  $5 \times 10^{-2}$  g per liter of the polymerization system. The ratio of the aluminum atoms to the transition metal atoms in the polymerization system is generally 4 to  $10^7$ , and preferably 10 to  $10^6$ .

In the process of the invention, the molecular weight

of the ethylene wax may be controlled by hydrogen and/or polymerization temperature. The polymerization temperature will generally be 20°C or above, preferably 40°C or above, and particularly preferably from 50 to 230°C. The hydrogen may  
5 be fed to the polymerization in an amount such that the molar ratio of the hydrogen to the ethylene will be 0.01 to 4, and preferably 0.05 to 2.

The polymerization by the process of the invention will be followed by the conventional treatment of the  
10 polymerization mixture to obtain the ethylene wax.

The ethylene wax prepared by the process is an ethylene homopolymer or an ethylene/ $\alpha$ -olefin copolymer. It has an intrinsic viscosity  $[\eta]$  of 0.4 dl/g or less, preferably from 0.005 to 0.35 dl/g, and particularly preferably from 0.01 to  
15 0.30 dl/g as measured in decalin at 135°C. The ethylene content in the ethylene wax generally ranges from 80 to 100 mol%, preferably from 85 to 100 mol%, and particularly preferably from 90 to 100 mol%. The  $\alpha$ -olefin content in the wax is generally in the range of 0 to 20 mol%, preferably 0 to 15 mol%,  
20 and particularly preferably 0 to 20 mol%. The ethylene wax generally has molecular weight distribution  $(\overline{M}_w/\overline{M}_n)$  of 3 or less, preferably 2.5 or less, and particularly preferably 2.0 or less according to gel permeation chromatography (GPC). The ethylene wax has 0 to 0.4, preferably 0 to 0.3 terminal



unsaturated bond per molecular chain thereof. Herein, the terminal unsaturated bonds are counted by IR method (e.g. one disclosed in Polym. Bull., 12, 111 (1984)).

[Effects of the invention]

5            Polymerization of ethylene or copolymerization of ethylene and other  $\alpha$ -olefin under catalysis by the transition metal compound and aluminoxane may yield ethylene wax even under low hydrogen partial pressure while suppressing the formation of by-product alkane to an extremely low level. The  
10 transition metal catalyst has high activity per unit quantity and allows efficient production of ethylene wax having narrow molecular weight distribution.

[Examples]

             Hereinbelow, the process of the invention will be  
15 described in greater detail by the following Examples.

#### Example 1

##### Preparation of aluminoxane

             A 400-ml flask sufficiently purged with argon was charged  
20 with 37 g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  and 125 ml of toluene with formation of a slurry. Subsequently, 0.5 mol of trimethylaluminum diluted with 125 ml of toluene was dropwise added to the slurry at temperatures of 0 to  $-5^\circ\text{C}$  over a period of 1 hour. After completion of the dropwise addition, the temperature was

raised to 40°C and reaction was carried out at the temperature for 24 hours. After the reaction, the solid and liquid were separated by filtration and the toluene was removed. As a result, 15 g of a white solid consisting of aluminoxane was obtained. Cryoscopy in benzene provided that the molecular weight of the aluminoxane was 1500. The aluminoxane had the integer  $m$  of 24. The aluminoxane was redissolved in toluene and used in polymerization.

#### Polymerization

10        A 1-L glass autoclave sufficiently purged with nitrogen was charged with 500 ml of refined o-xylene and the temperature was increased to 120°C. Subsequently, a mixed gas of ethylene and hydrogen was fed (at 100 l/hr and 40 l/hr, respectively). Thereafter, aluminoxane in an amount in terms of aluminum atom  
15    of 2.5 mg, and bis(cyclopentadienyl)zirconium dichloride in an amount in terms of zirconium atom of  $2.5 \times 10^{-3}$  mg were introduced, followed by polymerization at 120°C and atmospheric pressure for 1 hour. Polymerization took place in a uniform solution. After the polymerization, the polymer  
20    solution was poured into a large amount of methanol to precipitate the polymer. Overnight vacuum drying at 80°C gave polyethylene wax in a yield of 3.9 g. The catalytic activity in the polymerization was 1600 g polymer/mg zirconium atom. The polyethylene wax had an intrinsic viscosity  $[\eta]$  of 0.05

dl/g,  $\overline{M_w}/\overline{M_n}$  of 1.69, and an average of 0.07 terminal unsaturated bond per molecular chain thereof.

#### Example 2

5           Polymerization was carried out by the procedure illustrated in Example 1, except that the ethylene and hydrogen mixed gases were fed at 200 l/hr and 40 l/hr, respectively. Polyethylene wax was obtained in a yield of 7.2 g and had  $[\eta]$  of 0.07 dl/g and  $\overline{M_w}/\overline{M_n}$  of 1.76. The catalytic activity in the  
10       polymerization was 2900 g polymer/mg zirconium atom. The polyethylene wax had an average of 0.09 terminal unsaturated bond per molecular chain thereof.

#### Example 3

15           Polymerization was carried out by the procedure illustrated in Example 1, except that toluene was used as the solvent, the ethylene and hydrogen mixed gases were fed at 100 l/hr and 160 l/hr respectively, and the polymerization temperature and time were altered to 70°C and 1 hour.  
20       Polyethylene wax was obtained in a yield of 3.6 g and had  $[\eta]$  of 0.07 dl/g and  $\overline{M_w}/\overline{M_n}$  of 1.61. The catalytic activity in the polymerization was 1400 g polymer/mg zirconium atom. The polyethylene wax had an average of 0.03 terminal unsaturated bond per molecular chain thereof.

## Example 4

Polymerization was carried out by the procedure illustrated in Example 3, except that the ethylene and hydrogen mixed gases were fed at 200 l/hr and 160 l/hr, respectively. Polyethylene wax was obtained in a yield of 14.1 g and had  $[\eta]$  of 0.10 dl/g and  $\overline{M_w}/\overline{M_n}$  of 1.71. The catalytic activity in the polymerization was 5600 g polymer/mg zirconium atom. The polyethylene wax had an average of 0.05 terminal unsaturated bond per molecular chain thereof.

## Example 5

Polymerization was carried out by the procedure illustrated in Example 3, except that ethylene, propylene and hydrogen gases were fed at 200 l/hr, 20 l/hr and 140 l/hr, respectively. Ethylene/propylene copolymer wax was obtained in a yield of 9.8 g and had  $[\eta]$  of 0.08 dl/g,  $\overline{M_w}/\overline{M_n}$  of 1.84 and an ethylene content of 98 mol%. The catalytic activity in the polymerization was 3900 g polymer/mg zirconium atom. The ethylene/propylene copolymer wax had an average of 0.06 terminal unsaturated bond per molecular chain thereof.

## Example 6

A 2-L autoclave sufficiently purged with nitrogen was

charged with 1 liter of refined toluene and the temperature was raised to 165°C. Subsequently, the aluminoxane synthesized in Example 1 in an amount in terms of aluminum atom of 5.0 mg and bis(cyclopentadienyl)zirconium dichloride in an amount in terms of zirconium atom of  $1.5 \times 10^{-2}$  mg were forced into the autoclave with a mixed gas of ethylene and hydrogen (at 20 kg/cm<sup>3</sup> and 2 kg/cm<sup>3</sup>, respectively) to initiate polymerization. The polymerization was carried out at 170°C for 5 minutes and terminated with addition of ethanol. The polymerization was then followed by the same procedure as described in Example 1 to yield 87 g of polyethylene wax. The polyethylene wax had  $[\eta]$  of 0.15 dl/g and  $\overline{M}_w/\overline{M}_n$  of 2.42. The catalytic activity in the polymerization was 5800 g polymer/mg zirconium atom. The polyethylene wax had an average of 0.21 terminal unsaturated bond per molecular chain thereof.

#### Example 7

##### Preparation of aluminoxane

Aluminoxane was synthesized in the same manner as in Example 1, except that  $\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$  was used in 39 g and the reaction was carried out at 40°C for 6 days. Cryoscopy in benzene provided that the molecular weight thereof was 2800. The aluminoxane had the integer  $m$  of 46.

##### Polymerization

Polymerization was carried out by the procedure illustrated in Example 1 to yield 4.7 g of polyethylene wax. The polyethylene wax had  $[\eta]$  of 0.06 dl/g and  $\overline{M}_w/\overline{M}_n$  of 1.66. The catalytic activity in the polymerization was 1900 g  
5 polymer/mg zirconium atom. The polyethylene wax had an average of 0.06 terminal unsaturated bond per molecular chain thereof.

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